Small Angle Neutron Scattering Measurements of Asphaltene Nanoparticle Aggregation in Mixtures of Incompatible Crude Oils

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We study the structure and phase behavior of asphaltenes, comprised of large polyaromatic molecules, in mixtures of naturally-occurring crude oils using small angle neutron scattering (SANS). When two compatible oils are blended together, the asphaltenes remain colloidally dispersed. However, when two incompatible oils are blended together, the asphaltene nanoparticles can aggregate to form microscale structures over a limited range of volume fractions where the blend is dominantly paraffinic. We show that SANS directly probes asphaltene aggregation in unmodified (i.e. non-deuterated) crude oil mixtures due to a significant neutron scattering length density difference between the hydrogen-poor asphaltenes and the surrounding oil. Asphaltene aggregation and crude oil incompatibility can be identified by strong power law scattering at low wavenumbers and the depopulation of nanoscale asphaltenes, as evidenced by a departure of the structure factor of the nanoparticles from ideal behavior. Quantitative analysis of the SANS intensities from a systematically blended set of two incompatible oils over a wide range of mixing volume fractions simultaneously provides both the average size and concentration of nanoscale asphaltene particles and also the volume fraction of microscale asphaltene aggregates. We have also explored the role of the kinetics of asphaltene aggregation in incompatible crude oil mixtures using time-resolved SANS. These findings demonstrate that SANS is a useful technique for directly assessing the compatibility of crude oils and for diagnosing refinery fouling problems that can result from blends of incompatible oils.